

The Nature of the Pentafluorophenyl Grignard Reagent in Solution from Fluorine Magnetic Resonance Spectra

By D. F. EVANS and M. S. KHAN

(Department of Chemistry, Imperial College of Science, London)

It has been shown from *X*-ray measurements that solid phenylmagnesium bromide dietherate and ethylmagnesium bromide dietherate contain $\text{RMgBr}\cdot 2\text{Et}_2\text{O}$ units, with an approximately tetrahedral arrangement of groups around the magnesium.¹ However the nature of the Grignard reagents in solution is still uncertain. The application of n.m.r. spectra is severely limited by the

rapid exchange of alkyl or aryl groups which almost certainly occurs at room temperature.* Since the intermolecular exchange of the aryl groups is much slower in tris(pentafluorophenyl)-thallium than in triphenylthallium,⁶ the fluorine magnetic resonance spectra of pentafluorophenyl Grignard reagents have been studied.

In pentafluorophenyl derivatives, the resonance

* From proton chemical shift measurements, it was suggested that ethereal solutions of alkyl Grignard reagents should be formulated as $\text{R}_2\text{Mg}\cdot\text{MgX}_2$ rather than (solvated) RMgX (refs. 2, 3). Chemical (ref. 4) and spectroscopic (ref. 5) results show that "ethylzinc iodide" in ether and tetrahydrofuran solutions is, in fact, almost entirely present as EtZnI , although the proton resonance spectra of these solutions are almost identical with that of Et_2Zn (refs. 2, 4).

due to the *para*-fluorine normally is comparatively simple, consisting of a triplet with a spacing of

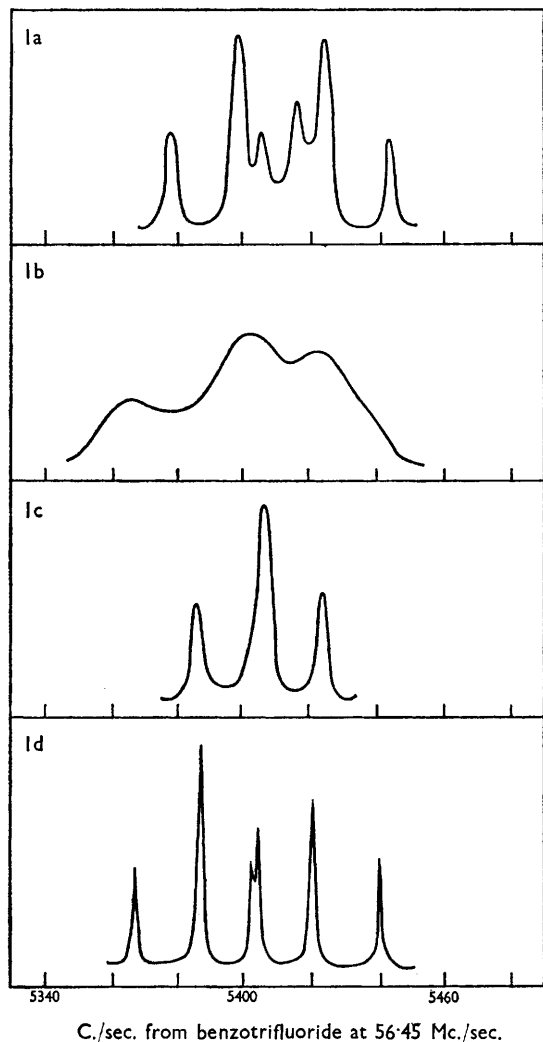


FIGURE 1. Fluorine resonance spectra (*para*-fluorine region) of 1 M-pentafluorophenylmagnesium bromide (a) at 22°, (b) at 45°, and (c) at 94°. (1d) 1 M-Pentafluorophenylmagnesium iodide at 22°.

* No other fluorine resonances could be detected, indicating that the Grignard reagent is formed almost quantitatively.

¹ R. E. Rundle and G. Stucky, *J. Amer. Chem. Soc.*, 1964, **86**, 4825; R. E. Rundle and L. J. Guggenberger, *ibid.*, p. 5344.

² D. F. Evans and J. P. Maher, *J. Chem. Soc.*, 1962, 5152.

³ W. Zeil and H. Roos, *Z. Electrochem.*, 1963, **67**, 28.

⁴ M. H. Abraham and P. H. Rolfe, *Chem. Comm.*, 1965, 325.

⁵ D. F. Evans and I. Wharf, *J. Organometallic Chem.*, 1966, **5**, 108.

⁶ D. F. Evans and M. S. Khan, unpublished work.

⁷ I. J. Lawrenson, *J. Chem. Soc.*, 1965, 1117.

about 20 c./sec. or a triplet of closely spaced triplets.⁷ An ethereal solution of bis(pentafluorophenyl)magnesium [prepared by the rapid and quantitative group exchange between $(C_6H_5)_2Mg$ and $(C_6F_5)_2Hg$ in ether] shows a single sharp *para*-triplet (spacing 19.2 c./sec.). Pentafluorophenylmagnesium bromide in ether (1 M) gives three regions of absorption (relative intensities 2:1:2) centred at ca. 50.8 p.p.m. (*ortho*-fluorines), ca. 95.9 p.p.m. (*para*-fluorine) and ca. 99.4 p.p.m. (*meta*-fluorines).^{*} In the *para*-fluorine region, two overlapping triplets of approximately equal intensity are observed at room temperature (Figure 1a). On heating this solution, these two triplets broaden and merge (Figure 1b) and finally at 95° a single sharp triplet is obtained (Figure 1c), indicating that there is an exchange between two species which has now become fast on an n.m.r. time-scale. Changes were also observed in the regions of absorption associated with the *ortho*- and *meta*-fluorines, but these were less characteristic. The chemical shifts of the two triplets are appreciably dependent on the concentration of the Grignard solution, although the chemical shift of the *para*-fluorine resonance in bis(pentafluorophenyl)magnesium is independent of concentration. Addition of bis(pentafluorophenyl)magnesium to an ethereal solution of pentafluorophenylmagnesium bromide increases the intensity of the high-field triplet relative to that of the low-field triplet. Accordingly the former can be assigned to $(C_6F_5)_2Mg$ or, more likely, to species based on this grouping such as $(C_6F_5)_2Mg \cdot MgBr_2$, which can presumably undergo rapid chemical exchange with $(C_6F_5)_2Mg$. The low-field triplet can then be assigned to C_6F_5MgBr , or to species based on this grouping. The spectrum of pentafluorophenylmagnesium iodide in ether at room temperature is similar to that of the bromide (Figure 1d), although here the low-field triplet has an appreciably higher relative intensity, and all the lines are sharper. For the bromide in tetrahydrofuran the high-field triplet is much more intense.

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